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Accurate Values for the Nonrelativistic Energies of the Lowest Singlet and Triplet S-States of the ^{4}He-Isotop

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Accurate lower and upper bounds for the nonrelativistic lowest energies $^1E_0$ and $^3E_0$ of the singlet and triplet-system of the ^{4}He-Isotop are calculated with the linearized method of variance minimization. The same was done for $^1E_1$ the energy of the first excited S-state 2^1S.

The results especially for $^1E_0$ and $^3E_0$ in a.u. are

$$-2.9033076997_5 \leq {}^1E_0 \leq -2.9033076921_8$$

$$-2.1749324263_7 \leq {}^3E_0 \leq -2.1749324245_9$$

i.e. the values are determined with an absolute error smaller than $0.00167\ \text{cm}^{-1}$ for $^1E_0$ and $0.00039\ \text{cm}^{-1}$ for $^3E_0$.

Key words: Eigenvalue problems, nonrelativistic energies of the ^{4}He-Isotop, nuclear motion.

1. Introduction

In a previous work [1] the groundstate energy $^1E_0$ of the He-atom in the infinite nuclear mass approximation was determined with an absolute error smaller than $0.0022\ \text{cm}^{-1}$. As mentioned but not explicitly explained the calculation in that paper was done with a Schrödinger operator transformed in symmetry adapted coordinates

$$u = y + z, \qquad v = y - z$$

using the notation as in [2].

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If the nuclear motion is taken into account the corresponding Schrödinger operator in these coordinates is

$$H = H^{(\infty)} + H^{(\kappa)}, \qquad H^{(\infty)} = H_0 + V$$

with

$$H_0 = \begin{cases} -\dfrac{\partial^2}{\partial x^2} - \dfrac{2}{x}\dfrac{\partial}{\partial x} - \dfrac{\partial^2}{\partial u^2} - \dfrac{4u}{u^2-v^2}\dfrac{\partial}{\partial u} - \dfrac{\partial^2}{\partial v^2} + \dfrac{4v}{u^2-v^2}\dfrac{\partial}{\partial v} \\ -\dfrac{2u(x^2-v^2)}{x(u^2-v^2)}\dfrac{\partial^2}{\partial x \partial u} + \dfrac{2v(x^2-u^2)}{x(u^2-v^2)}\dfrac{\partial^2}{\partial x\, \partial v} \end{cases}$$

$$V = \frac{1}{x} - \frac{8u}{u^2-v^2}$$

$$H^{(\kappa)} = \frac{1}{\kappa}\frac{4}{u^2-v^2}\left[(x^2-u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u} - (x^2-v^2)\frac{\partial^2}{\partial v^2} + 2v\frac{\partial}{\partial v}\right]$$

with

$$\kappa = 2\frac{m_k}{m_e} = 14698{,}36 \quad (m_k = m_{^4\mathrm{He}}).$$

These coordinates have the advantage that all integrals needed for the calculation of $\|H\psi\|^2$ and $(H\psi, \psi)$ have a remarkably simple form and could be expressed explicitly as it is shown in the appendix.

Because $\|H\psi_{prs}\| < \infty$ for the used basis functions

$$\psi_{prs} = x^p u^r v^s e^{-\alpha u}, \qquad \alpha > 0 \tag{1}$$

all $\psi_{prs} \in D_H$ with D_H as the domain of H.

2. The Calculation of the Eigenvalues

The determination of approximate values λ^* and the corresponding errors F^* for ${}^1E_0$, ${}^3E_0$ and ${}^1E_1$ was done with the linearized method of variance minimization and the Wieland iteration, which yields a very effective method for the calculation of the absolutely lowest eigenvalue. With the trick mentioned in [3] every isolated eigenvalue could be made the absolutely smallest.

In order to obtain good lower bounds Temple's formula

$$E_i \geq E_i^* = \lambda_i^* - \frac{F_i^*}{\rho_i - \lambda_i^*} \tag{2}$$

– notation as in [1] – was used for the lowest singlet- and triplet S-states as well as for the first excited S-state in the singlet system.

It has to be kept in mind that the application of Temple's formula demands a ρ_i with $E_i < \rho_i < E_{i+1}$ where E_{i+1} is the immediately following eigenvalue of E_i of H in the considered Hilbert-spaces. Remember that the singlet- and the

Table 1. The λ^*- and F^*-values for $^1E_0$, $^3E_0$ and $^1E_1$ of the ^{4}He-Isotop in a.u.

dim V_n	$^1\lambda_0^*$	$^1F_0^* \cdot 10^8$	$^3\lambda_0^*$	$^3F_0^* \cdot 10^8$	$^1\lambda_1^*$	$^1F_1^* \cdot 10^6$
203	-2.9033041944449_7	749.72600	-2.1749323642622_2	12.26050	-2.145483862_8	34.59500
308	-2.9033075120573_3	49.08290	-2.1749324223041_1	1.85902	-2.145656587_7	5.42210
444	-2.9033076823726_6	7.12253	-2.1749324244153_3	0.57123	-2.145678144_9	0.98774
615	-2.9033076913725_5	2.84683	-2.1749324244443_3	0.20895	-2.145680517_9	0.28778
825	-2.9033076920195_5	1.55938	-2.1749324245441_1	0.08399	-2.145680763_8	0.13317
946	-2.9033076921111_9	1.19075	-2.1749324245655_5	0.05483	-2.145680782_6	0.09791
1078	-2.9033076921362_2	0.92482	-2.1749324245784_4	0.03644		
1378	-2.9033076921827_7	0.57383	-2.1749324245916_6	0.01686		

Table 2. The λ^* and F^*-values for the 3^1S- and 3^3S-state in a.u.

	dim V_n	λ^*	$F^* \cdot 10^4$	$\lambda^* - \sqrt{F^*}$
3^1S	203	−2.0549	9.028	−2.085
3^3S	203	−2.0668	1.724	−2.080

triplet-states respectively are elements of separate symmetry adapted Hilbert-spaces in which the eigenvalue problem and Temple's formula can be formulated independently.

The method of variance minimization gives suitable ρ_i's if it is ensured that the error interval $[\lambda_i^* - \sqrt{F_i^*}, \lambda_i^* + \sqrt{F_i^*}]$ contains one eigenvalue only, which has to be E_i. In the case of the ^{4}He-Isotop the latter is guaranteed – for sufficient small F_i^* – by the knowledge of the correct sequence of the eigenvalues from spectral data [4]. Independently suitable ρ_i's can be chosen from lower bounds of the eigenvalues of the operator $H^{(\infty)}$, because it can be shown that $H^{(\kappa)}$ is a positive operator.

The results of the calculations of the λ_i^* values and corresponding errors F_i^* as a function of the dimension of the vectorspace V_n spanned by the ψ_{prs} with constant α's in (1) are shown in Table 1. The exponent α was chosen to $\alpha = 3.5$ for $^1\lambda_0^*$, $\alpha = 1.1$ for $^3\lambda_0^*$ and $\alpha = 1.65$ for $^1\lambda_1^*$.

Upper bounds for the E_i are the corresponding λ_i^*. The listing of the Ritz values λ^r [5] is omitted although they are calculated too. As a matter of fact they are rarely better than the corresponding λ^*'s but their errors are considerably worse than the minimal errors F^* obtained with the λ^*'s.

To get lower bounds for the E_i's the necessary ρ_i's were evaluated from rough λ^* and F^* values for the 3^1S- and 3^3S-states. Latter were calculated by matrix diagonalization with Householder's method. The results in a.u. are shown in Table 2.

With $^1\rho_1 = -2.085$, $^1\lambda_1^* = -2.145680782_6$ and $^1F_1^* = 9{,}791\ 10^{-8}$ we get the lower bound $^1E_1^* = -2.1456823_9$ from Eq. (2), i.e.

$$-2.1456823_9 \leq {}^1E_1 \leq -2.1456807_9$$

and $^1E_1$ is determined up to an absolute error smaller than 0.35 cm^{-1}.

With $^1\rho_0 = {}^1E_1^*$ and $^3\rho_0 = -2.080$ the bounds for $^1E_0$ and $^3E_0$ given above were calculated using the optimal λ^* – and F^* values taken from dim $V_n = 1378$.

3. The Influence of the Nuclear Motion for the 1^1S and 2^3S-State and the Comparison with the Experimental Data

The calculated eigenvalues E_i for the operator $H = H^{(\infty)} + H^{(\kappa)}$ of the ^{4}He-Isotop, where the nuclear motion ($H^{(\kappa)} \neq 0$) is taken into account from the beginning, together with the eigenvalues $E_i^{(\infty)}$ for $H^{(\infty)}$ and the experimental values of Herzberg [6] allow the discussion of two effects: first an accurate estimation of the influence of the nuclear motion, second the calculation of bounds for the relativistic corrections (including the Lamb-shift).

a) *Nuclear Motion*

The influence of the nuclear motion as a whole is given by the difference

$$\Delta_i = E_i - E_i^{(\infty)}.$$

Bounds for $^1\Delta_0$ and $^3\Delta_0$ are obtained from

$$E_0^* - \lambda_0^{*(\infty)} \leq \Delta_0 \leq \lambda_0^* - E_0^{*(\infty)}$$

with the lower and upper bound $^1E_0^{*(\infty)}$ and $^1\lambda_0^{*(\infty)}$ for $^1E_0^{(\infty)}$ from [1] in a.u.

$$-2.9037243866_6 \leq {}^1E_0^{(\infty)} \leq -2.9037243769_9$$

and the analog values for $^3E_0^{(\infty)}$ from the result of Pekeris [7]

$$-2.1752293810_0 \leq {}^3E_0^{(\infty)} \leq -2.1752293782_2.$$

We get

$$^1\Delta_0 = 91.452 \pm 0.002 \text{ cm}^{-1}$$

$$^3\Delta_0 = 65.173 \pm 0.002 \text{ cm}^{-1}.$$

Usually the nuclear motion is taken into account in the manner of Bethe and Salpeter [8], i.e. by the subsequent correction of the $E_i^{(\infty)}$ values, because only these values with the eigenfunctions $\psi_i^{(\infty)}$ are available from calculations in the infinite mass approximation. Apart from the fact, that the electron mass m_e is replaced by the reduced mass $\mu = m_e \cdot m_k / m_e + m_k$ an additional term, the mass-polarization $\varepsilon_m^{(i)}$ appears. Together with the approximated values

$$^1\tilde{\varepsilon}_m^{(0)} = 4.7854 \text{ cm}^{-1}, \qquad ^3\tilde{\varepsilon}_m^{(0)} = 0.2238 \text{ cm}^{-1} \tag{3}$$

from Pekeris [9] the "μ-correction" of $^1E_0^{(\infty)}$ and $^3E_0^{(\infty)}$ yields the following amounts for the nuclear motion

$$^1\tilde{\Delta}_0 = 91.490 \text{ cm}^{-1}, \qquad ^3\tilde{\Delta}_0 = 65.175 \text{ cm}^{-1}$$

obtained from

$$\tilde{\Delta}_i = \frac{m_k}{m_e + m_k} E_i^{(\infty)} + \tilde{\varepsilon}_m^{(i)} - E_i^{(\infty)} = -\frac{2}{2+\kappa} E_i^{(\infty)} + \tilde{\varepsilon}_m^{(i)}.$$

They are in good agreement with the correct Δ-values given above.

b) *The Relativistic Effects*

Experimental values for atomic energies are referred to the first ionization potential which was determined for the ^{4}He-Isotop by Herzberg [6] to

$$I.P.\,(^4\text{He}) = 198310.8_2 \pm 0.15 \text{ cm}^{-1}$$

In order to compare experimental with theoretical values the beginning of the continuum of the operator H has to be known. As was shown first by Žislin [10] for an atomic system the bottom of the continuum of H is identical with the groundstate of the operator for the corresponding ionic-system with the one electron less, i.e.

$$E_0^+ = \inf \sigma_c(H).$$

The groundstate energy of E_0^+ in a.u. for the $^4He^+$-ion is obtained to

$$E_0^+ = -2\frac{m_k}{m_e + m_k} = -2\frac{\kappa}{2+\kappa} = -1.999727898$$

if the finite nuclear mass of the ^4He is taken into account as against −2 a.u. for infinite mass.

With respect to E_0^+ the bounds for the nonrelativistic energies $\Delta E_i = E_i - E_0^+$ are

$$E_0^+ - E_i^* \le \Delta E_i \le E_0^+ - \lambda_i^*. \tag{4}$$

Since the experimental values from Herzberg [6] are obtained as wavenumbers ν_{exp} in cm^{-1} the bounds from (4) which are given in a.u. have to be converted into wavenumbers ν's via the Bohr radius $a_0 = \hbar^2/m_e e^2$.

This yields [11]

$$1 \text{ a.u.} \triangleq 219474.624 \pm 0.011 \text{ cm}^{-1}$$

where the uncertainty of 0.011 cm^{-1} of the conversion factor has to be taken into account and accepted too. The latter is not evident because it is almost beyond the accuracy of which the fundamental constant e, h and m_e are known.

The calculated bounds for the ν's and the experimental values $\nu_{\text{exp}}^{\pm}$ are shown in Table 3.

Bounds for the relativistic corrections (including the Lamb shift) are now obtained from

$$\overset{-}{\nu}_{\text{exp}} - \nu_{\text{max}} \le \delta_i \le \overset{+}{\nu}_{\text{exp}} - \nu_{\text{min}}.$$

We get in cm^{-1}

$$-2.177 \le {}^1\delta_0 \le -1.855, \qquad 1.730 \le {}^3\delta_0 \le 1.835.$$

Pekeris values (relativistic corrections E_j plus Lamb shift) ${}^1\tilde{\delta}_0 = -1.903 \text{ cm}^{-1}$ [9] and ${}^3\tilde{\delta}_0 = 1.813 \text{ cm}^{-1}$ [7] calculated with the wavefunctions $\psi_i^{(\infty)}$ from $H^{(\infty)}$ are in these limits.

Table 3. Values for $\nu_{\text{max}} = E_0^+ - E_0^*$, $\nu_{\text{min}} = E_0^+ - \lambda_0^*$ and $\nu_{\text{exp}}^{\pm}$ in cm^{-1}

	ν_{max}	ν_{min}	$\overset{+}{\nu}_{\text{exp}}$	$\overset{-}{\nu}_{\text{exp}}$
1^1S	198312.847	198312.825	198310.97	198310.67
2^3S	38452.950	38454.945	38454.78	38454.68

Appendix

Only three types of integrals are necessary for the calculation of $\|H\psi\|$ and $(H\psi, \psi)$. With the volume element

$$d\tau = \tfrac{1}{8}x(u^2 - v^2)\, dx\, dv\, du$$

and the region of integration

$$G: |v| \leq x \leq u, \qquad |v| \leq u, \qquad 0 \leq u \leq \infty$$

we have for $p = -1, 0, \ldots; r, s, = 0, 1, \ldots; q = p + r + s$

1. $$I_1 = \int_G x^p u^r v^s e^{-\alpha u}\, d\tau = \frac{(q+2)!}{(s+1)(s+p+2)} \alpha^{-(9+3)}$$

2. $p \neq -1$

$$I_2 = \int_G \frac{x^p u^r v^s}{u^2 - v^2} e^{-\alpha u}\, d\tau$$

$$= \frac{q!}{p+1} \alpha^{-q-1} \sum_{\nu=1}^{[p+1/2]} \frac{1}{p+s-2\nu+2} + \varepsilon_p \left[\ln 2 - \sum_{\nu=1}^{s} \frac{(-1)^\nu}{\nu} \right]$$

$\varepsilon_{2\mu} = 1$, $\varepsilon_{2\mu+1} = 0$, $[x]$ greatest whole number $\leq x$, $\sum_{\nu=1}^{0} \cdots = 0$.

3. $p = -1$

$$I_3 = \int_G \frac{u^r v^s}{x(u^2 - v^2)} e^{-\alpha u}\, d\tau = q!\alpha^{-q-1} \left[\frac{\pi^2}{8} - \sum_{\nu=1}^{s} \frac{1}{(2\nu - 1)^2} \right]$$

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